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A STUDY OF HEXAGONAL AND CUBIC ICE AT LOW TEMPERATURES

by

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PREFACE

This report was prepared by Dr. Motoi Kumai, Research Physicist, Physical Sciences Branch, Research Division (James A. Bender, Chief), U. S. Army Cold Regions Research and Engineering Laboratory.

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SUMMARY

The formation of hexagonal and cubic forms of ice was studied by the use of a cold stage in an electron microscope within the temperature range -90 to -180C.

Ice crystal specimens were made on cold substrates, i.e., a collodion film, gold foil, or copper grid on the specimen holder of the cold stage. The structural forms of the ice were detected with the electron microscope using the selected area electron diffraction method.

The hexagonal form of ice formed on the cold substrates at temperatures from -90 to -100C. At -100 to -130C, both hexagonal and cubic forms of ice were detected. From -130 to -160C only cubic ice was found. At temperatures below -160C, minute crystals of cubic ice were detected.

No transformation of the structural form of ice from hexagonal to cubic or from cubic to hexagonal occurred when the temperature of the specimens was varied in the range -90 to -160C. The minute crystals of cubic ice formed below -160C were transformed into larger cubic ice crystals by heating them to a temperature between -130 and -150C. The lattice constants of hexagonal and cubic ice, and the coefficient of thermal expansion of ice were calculated from the experimental results.

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INTRODUCTION

Investigations of the structural form of ice sublimed from water vapor onto a cold substrate have been carried out by many investigators using different methods, i.e., X-ray diffraction, electron diffraction, calorimetry, and electron microscopy using the selected area diffraction method.

When water vapor sublimed on a base at a temperature above -85C, the X-ray pattern of the ice was found to be normal hexagonal by Burton and Oliver (1935). At temperatures below -110C, the pattern consisted of two diffuse lines; ice demonstrating such characteristics was described as vitreous ice.

A determination of the lattice constants of hexagonal ice at -66C was made using the X-ray diffraction method by Megaw (1934) with the results:

$$a = 4.5085 \text{ X.U. } (4.5176 \pm 0.0001 \text{ Å})$$

$$c = 7.338 \text{ X.U. } (7.3528 \pm 0.0002 \text{ Å}).$$

From these measurements the ratio c/a is 1.628, which does not agree with the value for close packing (1.633).

An investigation of the cubic and hexagonal forms of ice was carried out by König (1943) using the electron diffraction method. Ice specimens were formed on a thin collodion film in a low-temperature unit designed for transmission experiments with an electron-diffraction camera. The temperature of the specimen was controlled by a heater in the apparatus. The ice specimen formed at -170C gave a diffraction pattern of diffused rings. When the specimen was heated to about -140C, ring patterns characteristic of the diamond-type cubic structure were obtained. The lattice constant of the cubic ice was calculated to be 6.36 ± 0.01 Å. The specimen formed at about -80C produced the electron diffraction ring pattern of hexagonal ice.

Honjo et al. (1956) designed a cold stage for electron diffraction analysis of the structure of ice formed at temperatures from -70 to -170C. The ice specimens were formed on a cooled collodion film on a grid in the cold stage by injecting water vapor from a glass tube containing moisture-laden silica gel. The transmission diffraction patterns of hexagonal ice were obtained above -80C. Ice specimens formed at -150C showed the ring patterns of cubic structure. Ice formed below -160C was found to give diffuse halo patterns. The (222) ring from cubic ice and the corresponding (00.4) ring from hexagonal ice were observed. It is suggested that when the scattering by hydrogen atoms in Pauling's position is taken into account, the observed intensity of the rings agrees well with the calculated value.

Blackman and Lisgarten (1957), using both transmission and reflection electron diffraction, observed three types of diffraction patterns, the type depending on the temperature of the substrate, a cooled collodion film or silver film. Below -140C diffused rings were obtained. Between -140 and -120C a sharp ring pattern characteristic of the diamond-type cubic pattern was observed. Between -120 and -100C a sharp ring pattern of both the hexagonal and cubic ice types was found, and above -100C only the hexagonal pattern was produced. The lattice constants of the hexagonal ice were calculated to be

$$a = 4.493 \pm 0.004 \ \text{Å} \quad \text{and} \quad c = 7.337 \pm 0.006 \ \text{Å}, \ \text{at} \ -110\text{C}$$

and that of the cubic ice was

$$a = 6.350 \pm 0.008 \ \text{Å}, \ \text{at} \ -130\text{C}.$$

Ice crystals of sub-micron diameter were first observed by Hall (1950) using the replica method, and then by Hibi and Yada (1959) using an electron microscope. The first direct observation of ice crystals formed on a cooled Formvar film at temperatures from -70 to -120C was made by Fernandes-Moran (1960), who was also the first to obtain the Moire pattern exhibited by hexagonal ice crystals grown on a single-crystal film of mica at -80C. Vertsner and Zhdanov (1965) also made direct observations of ice crystals and the electron diffraction ring pattern of hexagonal, cubic and amorphous forms of ice at temperatures from -70 to -160C.

This paper presents the results of measurements of the lattice constants and coefficients of thermal expansion of ice crystals, and reports on the temperature dependency and the transformation of the structural form of ice.

EXPERIMENTAL PROCEDURE AND SPECIMEN PREPARATION

An EMU-3G cold stage and RCA electron microscope were used for this research. The heat exchange for the cooling system was built into the specimen chamber of the microscope. The specimen was cooled to -180C by the use of liquid nitrogen. Intermediate specimen temperatures were provided by the cold stage heater. The temperature was measured at the specimen by means of a ring-shaped thermocouple consisting of a copper-stainless steel junction formed during construction of the bi-metal specimen holder. The specimen rested against the thermal junction. A microvolt meter, calibrated at 0C and at -196C, the boiling point of liquid nitrogen at 1 atm pressure, was used to measure the temperature. The vacuum of the electron microscope was measured by an ionization gauge.

The ice crystal specimens were formed on the surface of a collodion film, a thin foil of gold, a thin cleavage surface of mica, or a grid of copper on the specimen holder of the cold stage. The surface to be used for ice crystal formation was cooled to the desired temperature of less than -90C in pure nitrogen gas at atmospheric pressure. A steep temperature gradient existed on the surface of the specimen holder. A small amount of water vapor was introduced into the specimen holder, causing minute droplets to form above its surface. The ice crystal specimens grew on the surface of the cold substrates by sublimation of water vapor from the minute droplets. Ice crystal photomicrographs and their electron diffraction patterns were obtained with the electron microscope in the temperature range -90C to -180C with a 10^{-4} to 10^{-5} mm Hg vacuum.

MEASUREMENT OF LATTICE CONSTANTS

The lattice constants of the hexagonal and cubic ice crystals were determined by comparing their patterns with those from a standard substance, sodium chloride or gold, which was shadowed in a vacuum chamber on one part of a thin collodion film on the electron microscope grid. At room temperature the electron diffraction pattern of this substance was recorded on a photographic plate. Ice crystals were then formed on the filmed grid at temperatures from -90 to -180C. An ice pattern and a combined pattern of ice and standard substance were made on photographic plates by a slight shift of the grid.

The camera constant λL can be obtained for the standard substance by the relation of a Bragg reflection,

$$\lambda L = rd$$

where d (Å) is the spacing of the h k l plane, r (cm) is the radius of the ring pattern from the hkl plane, λ (Å) is the electron wave length, and L (cm) is the camera length.

The d-spacings can be obtained from the accurately known value of the lattice constant of sodium chloride, a = 5.601 ± 0.003 Å at -130C (Blackman and Lisgarten, 1957). This value was in good agreement with that obtained by estimation based on thermal data using the Gruneisen formula.

Once λL is determined for the standard ring pattern, the d-spacing of the specimen can be obtained by dividin[illegible] λL by the measured radius r of the ring patterns for the specimen. The ra[illegible]s values are based on eight determinations of each ring diameter, each being taken twice at 45° intervals. The observed value of λL for the standard substance, the average measured values of 2r for each ring pattern from the ice, and the calculated values of the lattice constant for hexagonal and cubic ice are tabulated in Table I.

Table I. Determination of lattice constants.

Hexagonal ice at -110C λL = 4.2931 (A cm)				Cubic ice at -130C λL = 4.5129 (A cm)		
Ring index	2r(cm)	a(Å)	c(Å)	Ring index	2r(cm)	a(Å)
10.0	2.203	4.499	--	111	2.456	6.365
00.2	2.340	--	7.338	220	4.023	6.346
10.1	2.492	(4.504)	(7.371)	311	4.716	6.348
10.2	3.207	(4.513)	(7.365)	331	6.181	6.366
11.0	3.811	4.505	--	422	6.965	6.349
10.3	4.139	(4.506)	(7.351)			
11.2	4.474	(4.500)	(7.347)			
12.0	5.831	4.499	--			
30.0	6.612	4.498	--			
30.2, 10.6	7.003	4.505	7.357			

Average a = 4.501 ± 0.004 Å
c = 7.348 ± 0.009 Å
c/a = 1.633

Average a = 6.355 ± 0.01 Å

The values of the lattice constants were:

a = 6.355 Å at -130C for cubic ice
a = 4.501 Å at -110C for hexagonal ice
c = 7.348 Å at -110C for hexagonal ice
c/a = 1.633 at -110C for hexagonal ice.

In the case of the hexagonal ice crystals, the a spacing was measured from four patterns of 10.0, 11.0, 12.0 and 30.0 rings which did not involve the c spacing. The c spacing was determined from the measurement of the combined patterns of the 00.6 and 30.2 rings, and the 00.2 ring (Table I). The temperature of the specimens was measured within an error of about 5C by the calibrated copper-stainless steel thermocouple.

In this experiment lattice spacings of hexagonal ice for high indices such as 10.6, 11.6, 31.2, and 31.3 were observed for the first time (Table II).

Table II. Interplanar distances for hexagonal and cubic ice. *

Hexagonal ice at -110C				Cubic ice at -130C			
hkl	d(Å) calc	d(Å) obs	Intensity obs	hkl	d(Å) calc	d(Å) obs	Intensity obs
10.0	3.898	3.919	very strong				
00.2	3.674	3.676	very strong	111	3.670	3.690	very strong
10.1	3.446	3.450	very strong				
10.2	2.674	2.665	medium				
11.0	2.251	2.263	very strong	220	2.246	2.249	strong
10.3	2.074	2.075	strong				
20.0	1.949	1.963	weak				
11.2	1.919	1.926	strong	311	1.916	1.925	medium
20.1	1.884	1.884	weak				
00.4	1.837	1.838	very weak	222	1.834	1.840	very weak
20.2	1.722	1.715	weak				
				400	1.593	1.591	very weak
20.3	1.525	1.514	medium				
12.0	1.473	1.471	medium				
				331	1.458	1.455	medium
12.1	1.445	1.437	medium				
12.2	1.367	1.362	medium				
30.0	1.299	1.299	medium	422	1.297	1.304	medium
12.3	1.263	1.261	medium				
30.2 00.6	1.225	1.228	weak	511 333	1.223	1.217	weak
10.6	1.168	1.166	weak				
22.0	1.125	1.128	weak				
11.6	1.075	1.068	weak				
31.2	1.037	1.036	weak				
31.3	0.989	0.983	very weak				

* Calculated values for lattice spacings are based on a = 6.3546 Å for cubic ice at -130C and a = 4.501 Å, c = 7.348 Å for hexagonal normal ice at -110C.

Most of the observed ring patterns of the diamond-type cubic ice coincide within the error of observation with the ring patterns of the hexagonal ice. In the examination of many diffraction patterns, very weak traces of the (400) and (222) ring patterns from cubic ice, and the (00.4) ring pattern from hexagonal ice, were observed.

DIFFRACTION PATTERN AND GRAIN SIZE OF ICE

A large number of hexagonal crystals with diameters of 0.1 to 2.0μ, with the most frequently occurring diameter 0.3μ, were formed on copper grids previously cooled to -100C. The basal and prismatic planes were revealed upon examination (Fig. 1a). The average height of the hexagonal crystals was about

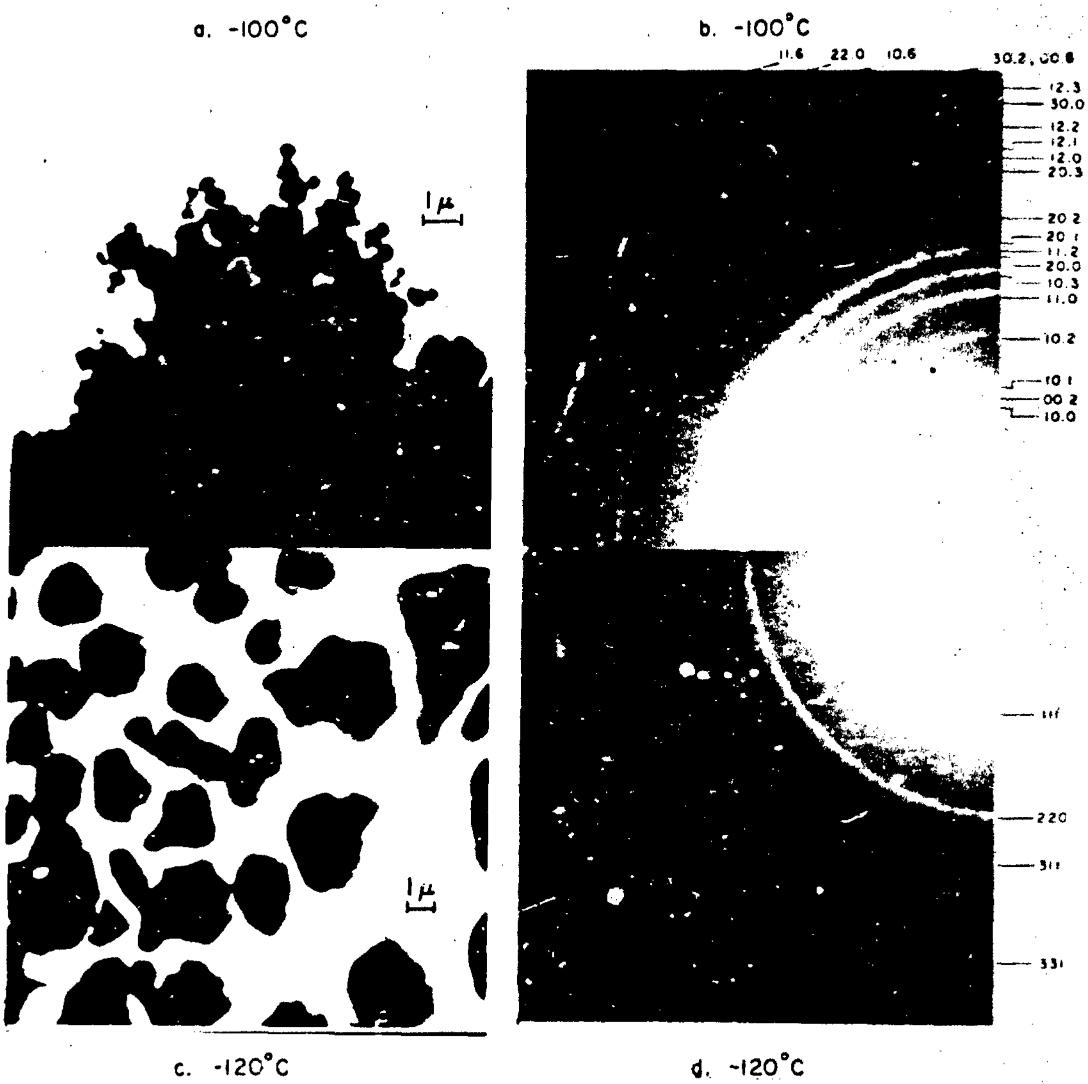


Figure 1. (a) Hexagonal ice crystals formed on a copper grid at -100C; (b) their hexagonal ring patterns. (c) Hexagonal and cubic ice crystals formed on a collodion film at -120C; (d) spot patterns from the hexagonal ice and sharp rings from the cubic ice shown in (c).

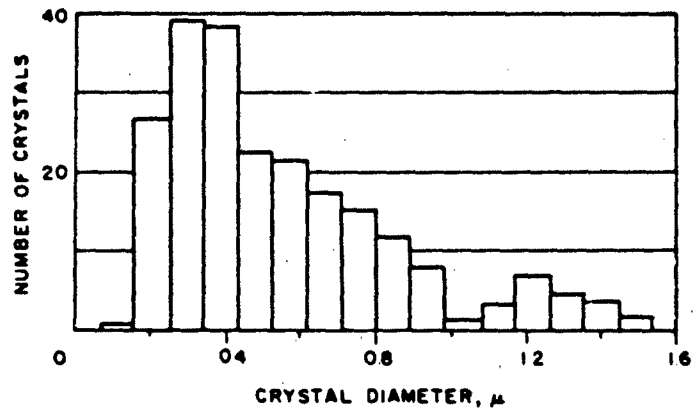


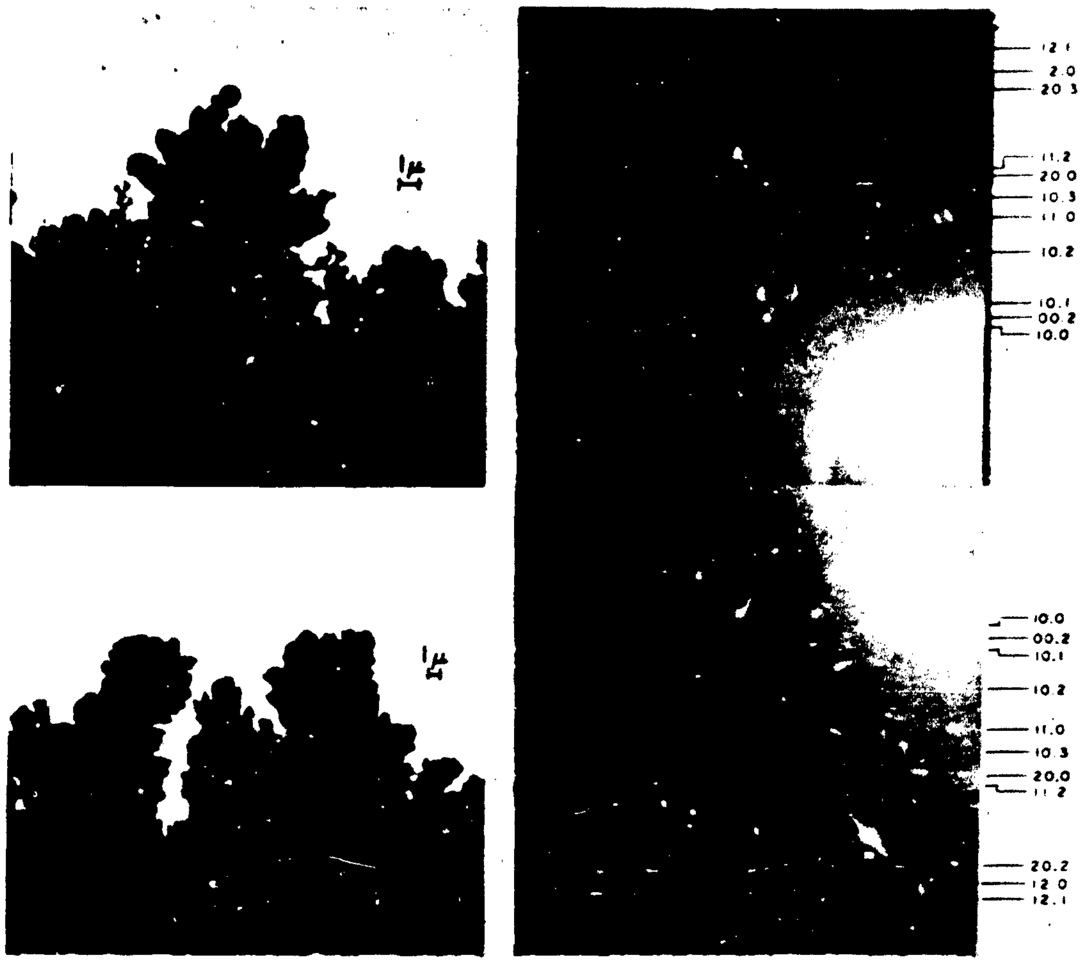
Figure 2. The size distribution of the ice crystals shown in Figure 1a.

0.7 of the diameter of the hexagonal base. This is close to the value 0.8 obtained by Krastanov (1943) and Wolf (1957) for an equilibrium form of hexagonal ice when only the interaction between the nearest oxygen neighbors was taken into consideration.

Transmission electron diffraction patterns for ice crystals of known size distribution (Fig. 2) were observed. The width of the diffraction ring depends on the grain size of the ice crystals, the camera length, the diameter of the electron beam, amount of electron beam adsorption by ice, etc. Using about 20μ beam diameter and $50\mu^2$ of selected area, the transmission electron diffraction pattern of hexagonal ice in the diameter range 0.1 to 2.0μ, with most frequently occurring diameter 0.3μ (Fig. 1a), showed ring patterns with some spots in the ring (Fig. 1b). Ice crystals larger than 1μ diam showed spot patterns. When the most frequently occurring diameter was larger than 0.3μ, the spot pattern was more prominent and the ring patterns became faint (Fig. 3a, b). With further growth of the $>0.3\mu$ crystals in the direction of the electron beam, the characteristic needle-like patterns of electron diffraction were observed (Fig. 3c, d). Minute crystals, possibly around 500 Å diam, gave sharp ring patterns (Fig. 4b), and minute crystals less than 100 Å diam gave broad diffraction rings (Fig. 4d) as was observed by Vertsner et al. (1965).

In an examination of many diffraction plates, faint traces of the (00.4) ring of the hexagonal ice were observed in some plates, and very weak traces of (400) and (222) ring patterns from cubic ice were present. The observed lattice spacings of the hexagonal ice (Fig. 1a) are shown in Table II.

a. -110°C b. -110°C



c. -110°C d. -110°C

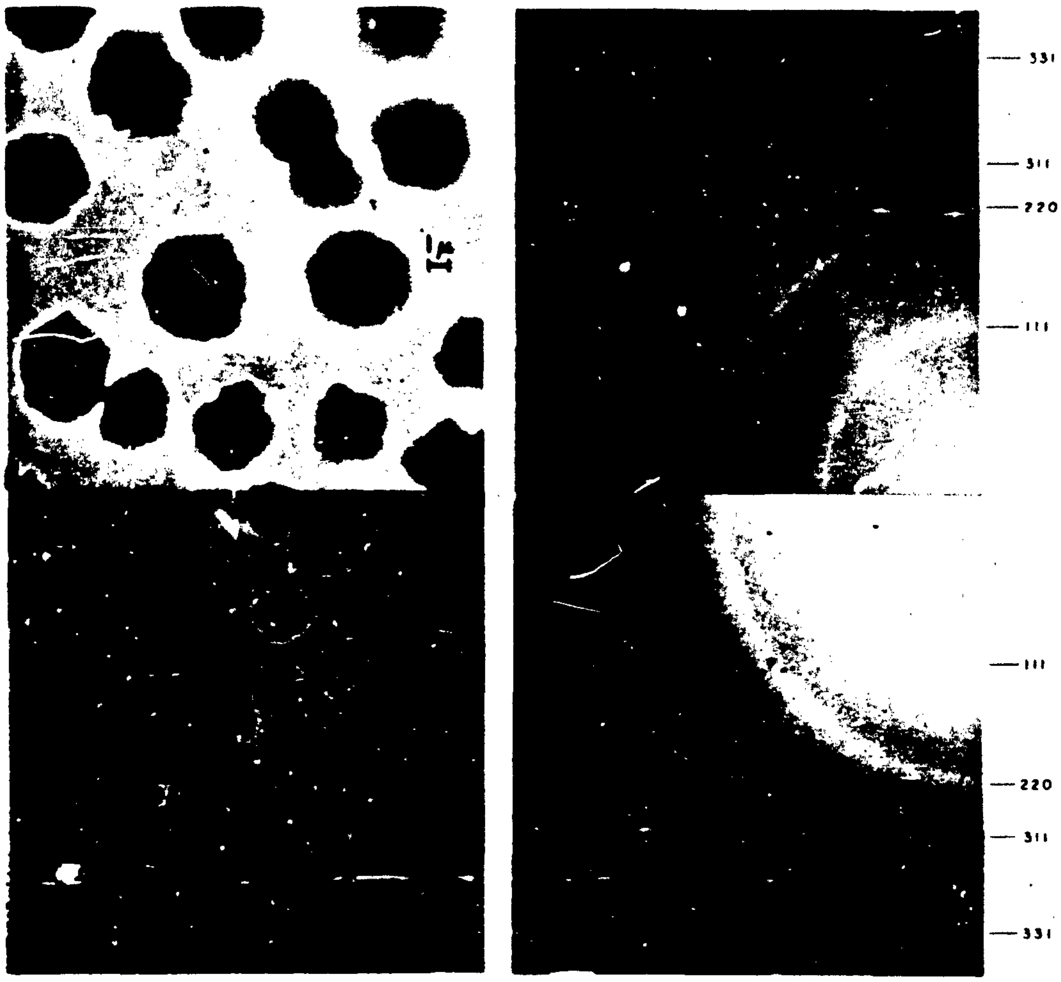
Figure 3. (a) Hexagonal ice crystals grown on a copper grid at -110C; (b) electron diffraction pattern of (a) showing prominent spots and faint rings. (c) Hexagonal crystals grown further in the direction of the electron beam; (d) the characteristic needle-like patterns of the electron diffraction of (c).

REPLICATION OF CRYSTALS BY CONTAMINATION

Ice crystals that form from residual water vapor in the electron microscope are contaminated by oil vapor from the microscope's oil diffusion pump. When one of these crystals sublimes, the residue retains the shape of the original crystal, forming a replica which may be viewed at room temperature in the microscope. As seen in photomicrographs (Fig. 4a, c) these crystal replicas have transparent edges, possibly due to migration of contaminating particles within the original crystals.

a. From -120°C to -140°C

b. At -140°C



c. From -130°C to -170°C

d. At -170°C

Figure 4. Ice crystals and replicas formed on a collodion film (a, c) and their electron diffraction patterns (b, d) respectively.

TEMPERATURE DEPENDENCY OF THE STRUCTURAL FORM OF ICE

A series of experiments was carried out on crystals formed at temperatures from -90 to -180C to determine the structural forms present at these temperatures. At temperatures above -100C hexagonal crystals formed (Fig. 1a, b). At -120C both hexagonal and cubic ice formed on the collodion film. The cubic crystals were detected by their electron diffraction patterns. The hexagonal ice crystals grew to a size of 1 to 3μ diam, and the cubic crystals grew to a size less than 0.1μ diam (Fig. 1c). The rate of growth of the hexagonal crystals was more than 10 times greater than that of the cubic crystals at -120C. The cubic ring patterns from {111}, {220}, {311} and {331} and the spot patterns from the hexagonal crystals are seen in Figure 1d.

The residual water vapor in the electron microscope was condensed at -140C on the collodion film with replicas of the ice crystals previously formed by contamination in the electron microscope. Cubic crystals could not be detected at 3000X magnification (Fig. 4a) but the electron diffraction patterns showed {111}, {220}, {311} and {331} cubic diffraction rings (Fig. 4b). At -170C no cubic crystals were visible (Fig. 4c) but again the cubic ring patterns appeared (Fig. 4d), although the rings were more diffuse than those at -140C. It is concluded that a very minute form of crystalline cubic ice is present at -170C.

These experiments have shown that the structural form of the ice depends on the temperature of the substrate on which it forms. The four types of electron diffraction patterns produced by ice at temperatures from -100 to -180C are shown in Table III, and the results of experiments by many workers (as well as those reported here) on the temperature dependency of the structural form of ice at low temperatures are summarized in Table IV.

Table III. Types of electron diffraction patterns of ice crystals formed at various temperatures.

Temperature of base °C	Type of pattern
> -100	Sharp rings of hexagonal ice
-100 to -130	Sharp rings of both hexagonal and cubic ice
-130 to -160	Sharp rings of cubic ice
-160 to -180	Diffused rings of minute cubic ice

Table IV. Temperature dependency of the structural form of ice crystals formed at low temperatures.

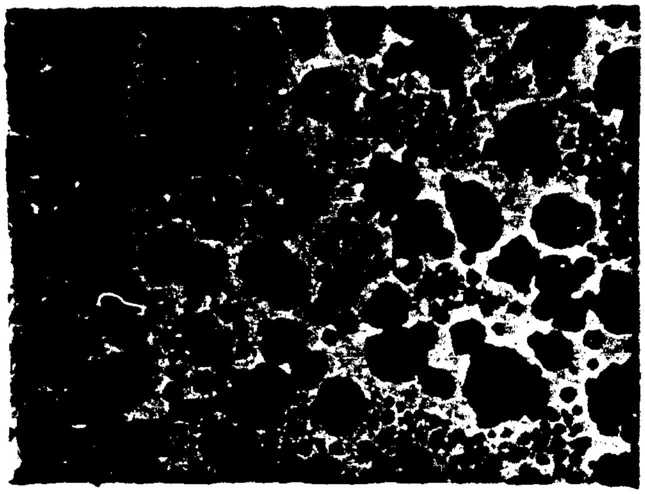
Experimental method	-180	-170	-160	-150	-140	-130	-120	-110	-100	-90	-80	-70	Reference
X-ray diffraction				amorphous					semi-crystalline		hexagonal		Burton and Oliver (1935)
Electron diffraction		small crystals				cubic						hexagonal	König (1943)
Calorimetric				amorphous					crystalline				Pryde and Jones (1952)
Electron diffraction		amorphous or minute crystals					cubic					hexagonal	Honjo *et al.* (1956)
Electron diffraction			amorphous or small crystals			cubic		hexagonal and cubic			hexagonal		Blackman and Lisgarten (1957)
Electron microscope and electron diffraction								cubic			hexagonal		Fernandes-Moran (1960)
Electron microscope and electron diffraction			amorphous			cubic			hexagonal				Vertsner *et al.* (1964)
Electron microscope and electron diffraction		minute cubic crystals			cubic			hexagonal and cubic			hexagonal		Kumai (1966) (this paper)

TRANSFORMATION OF THE STRUCTURAL FORM

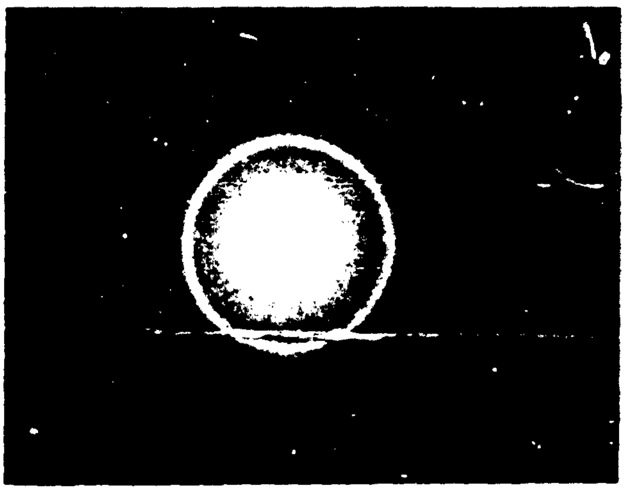
Transformation of the structural form of the ice by temperature change was examined by comparing the electron diffraction patterns of the ice before and after the temperature change.

When hexagonal ice crystals that were produced at -90C were cooled to -140C, the temperature of cubic ice formation, no change in structural form was noted even after about an hour at the lower temperature.

Similarly, the combination of hexagonal and cubic ice which was formed at -120C did not change structure when cooled to -170C (Fig. 5a, b).



a. Specimen temperature changed from -120C to -170 C.



b. Diffraction pattern at -170C.

Figure 5. Ice crystals formed on a collodion film (a), and their electron diffraction pattern (b).

Ice crystals formed at -170C on collodion film under a poor water vapor supply condition by residual water vapor in the electron microscope showed diffused ring patterns corresponding to the {111}, {220}, {311} and {331} rings of cubic crystals (Fig. 4c, d). These were microcrystalline cubic crystals. When these minute crystals were warmed to -140C, the rings appeared sharper because of the growth of the crystals but the same rings were observed, indicating no structural transformation. The results of this experiment are tabulated in Table V along with results of Honjo et al. (1956) and Vertsner et al. (1965). It was found that cubic ice crystals are formed below -100C at a lower rate of growth than that of the hexagonal ice; minute cubic ice was detected even at -170C; and no transformation of the structural form was observed after the specimen temperature was changed.

Table V. Transformation of structural form of ice by temperature change.

Initial temp ice formed (°C)	Final ice temp (°C)	Change of structural form of ice	Observer
-160	-150	From minute crystalline or amorphous to cubic	Honjo et al.
-160	-140	From minute crystalline or amorphous to cubic	Vertsner and Zhdanov
-170	-140	Cubic - no change of structural form	Kumai (this paper)
-140	-170	Cubic - no change of structural form	Kumai (this paper)
-140	- 80	Cubic - no change of structural form	Vertsner and Zhdanov
- 80	-150	Hexagonal - no change of structural form	Honjo et al.
- 90	-140	Hexagonal - no change of structural form	Kumai (this paper)
- 90	-160	Hexagonal - no change of structural form	Kumai (this paper)
-120	-170	Hexagonal and cubic - no change of structural form	Kumai (this paper)

THERMAL EXPANSION OF ICE

The coefficient of linear expansion of polycrystalline bulk ice was determined by Jakob and Erk (1928) in the temperature range 0 to -240C. The measurements were made on rod-shaped ice frozen slowly in paper tubes from the outside in. The ice showed no indication of any regular orientation of the crystal axes.

The coefficient of expansion for ice can be calculated from the lattice constants obtained at various temperatures (Table VI). The lattice constants of hexagonal ice were measured by several workers by diffraction methods at temperatures between 0 and -180C. The lattice constants measured in the present experiments and by Blackman and Lisgarten (1957) made use of electron diffraction techniques. Others listed in Table VI used the X-ray diffraction method. The discordance of the data in Table VI, which may be due to the different forms of the specimens, has been noted by Lonsdale (1958), who desired a new determination with the same kind of specimen varied over a wide range of temperatures.

Comprehensive low temperature measurements were made by LaPlace and Post (1960) with a Geiger counter diffractometer. Specimens were prepared on a cooled glass specimen holder by spraying a fine mist of distilled water. The specimens were warmed up to just below the melting point and then cooled slowly down to a certain temperature to get sharp diffraction for lattice constant measurements. The c/a ratio of the ice formed from fine mist was smaller than that of the ideal value of 1.633 for close packing. The ice may have unequivalent tetrahedral bonds, i.e., the hydrogen bond along the c-axis might be slightly shorter than the centro-symmetric hydrogen bonds or, alternatively, the 0-0-0 angles may differ slightly from the exact tetrahedral value. However, the c/a ratio was 1.633 in this experiment and for the experiments of Blackman and Lisgarten (1957) for ice formed from vapor at an air temperature of approximately -100C and a low vapor pressure of about 10^{-5} mm Hg.

The density and the coefficient of expansion of ice can be found from the unit cell parameters obtained at various temperatures from 0 to -180C (Table VII). The values given in Table VII were obtained from the curves of unit cell parameters shown in Figure 6 by taking the molecular weight of ordinary water as 18.016, and Avogadro's number as 6.02486×10^{23} (Cohen and DuMond, 1956). The coefficients of cubical and linear expansion of hexagonal ice are shown in Figure 7 along with the results of other workers. The coefficient of linear expansion along the c-axis is almost the same as that of the a-axis. Therefore, it is almost the same as that of polycrystalline ice as determined by Jakob and Erk (1928).

Table VI. Lattice constants of hexagonal ice.

Temp (°C)	a(Å)	c(Å)	c/a	Reference
0	4.5227 ± 0.0014	7.3671 ± 0.0012	1.629	Megaw (1934)
-40.5	4.511 ± 0.001	7.345 ± 0.001	1.628	Camp (1963)
-46	4.5163 ± 0.0005	7.3477 ± 0.0009	1.627	Truley (1955)
-110	4.493 ± 0.004	7.337 ± 0.006	1.633	Blackman and Lisgarten (1957)
-110	4.501 ± 0.004	7.348 ± 0.009	1.633	Kumai (this paper)
-185	4.479	7.308	1.632	Vegard and Hillesund (1942)

Table VII. The unit-cell parameters, the densities, and the coefficients of expansion of ice at 1 atm pressure.

Temp (°C)	Unit cell parameters a (Å)	c (Å)	c/a	Density (calc) (g/ml)	Coefficients of expansion Linear ($\alpha_a \times 10^6$)	($\alpha_c \times 10^6$)	Cubical ($\beta \times 10^6$)
0	4.5227	7.3671	1.6289	0.9166			
					47	48	142
- 30	4.5163	7.3565	1.6288	0.9205			
					47	47	141
- 60	4.5099	7.3461	1.6288	0.9244			
					41	37	117
- 90	4.5044	7.3379	1.6290	0.9277			
					34	35	102
-120	4.4998	7.3302	1.6290	0.9306			
					28	28	83
-150	4.4960	7.3240	1.6290	0.9329			
					22	20	63
-180	4.4930	7.3196	1.6290	0.9348			

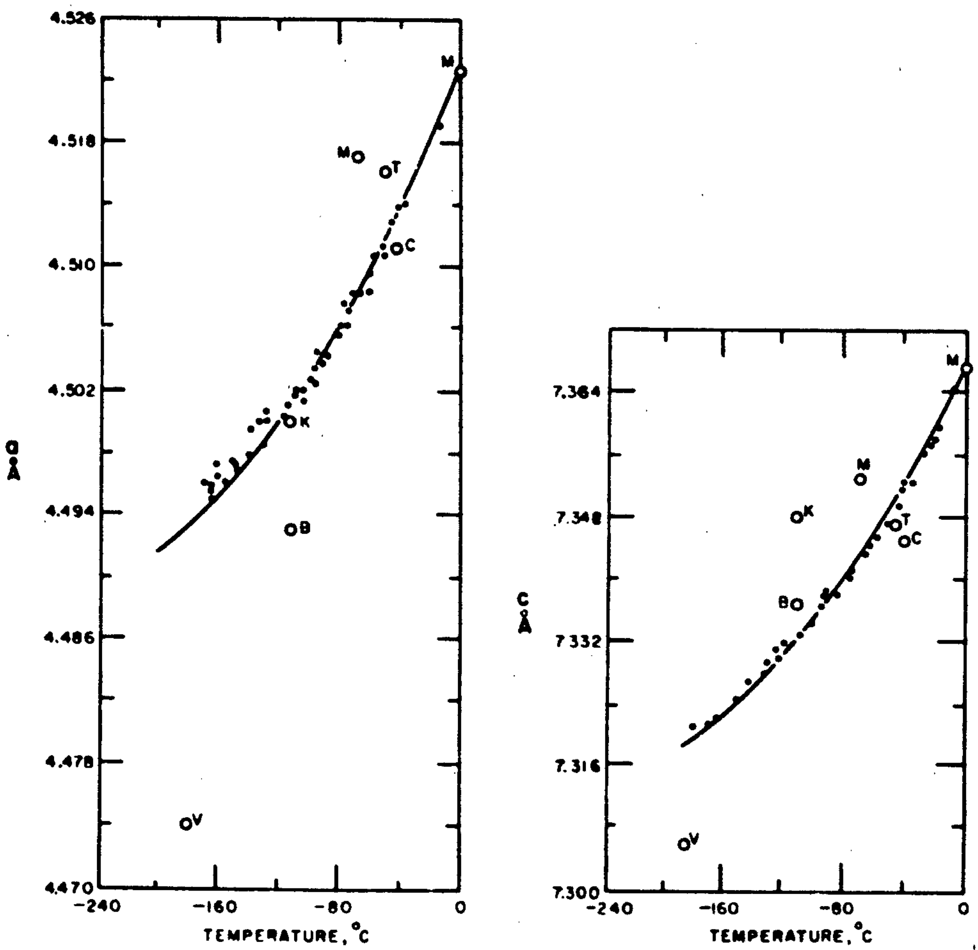


Figure 6. Unit cell parameters of hexagonal ice determined by LaPlace and Post (·), Megaw (M), Truley (T), Camp (C), Kumai (K), Blackman and Lisgarten (B), and Vegard and Hillesund (V).

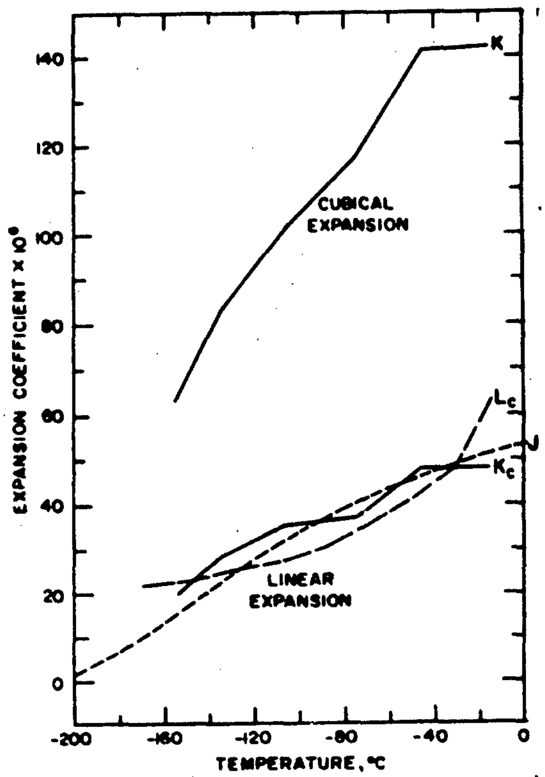


Figure 7. The coefficient of thermal expansion of hexagonal ice by Kumai (K; Kc along the c-axis), LaPlace et al. (Lc along the c-axis), and Jakob et al. (J, polycrystalline ice).

SUMMARY AND CONCLUSIONS

The formation and lattice spacing of hexagonal and cubic forms of ice crystals were observed by the use of a cold stage in an electron microscope within the temperature range -90 to -180C.

Hexagonal ice formed on the cold substrates at temperatures above -100C. At temperatures from -100 to -130C, both hexagonal and cubic forms of ice were detected. Cubic ice was formed on cold substrates from -130 to -160C. At temperatures below -160C, the minute form of cubic crystalline ice was detected. It is concluded that ice crystal formation depends on the temperature and the crystal habit of the substrate.

No transformation of the structural form of ice from hexagonal to cubic or cubic to hexagonal was observed when the temperature of the specimens was varied in the range -90 to -180C. The minute crystalline cubic ice formed below -160C grew larger at a temperature between -130 and -150C, displaying the sharp diffraction patterns of cubic ice.

Single ice crystals larger than 0.3μ diam produced diffraction spot patterns. Many ice crystals less than 0.3μ diam produced uniform sharp ring patterns. Ice crystals less than 50 Å in diameter produced halo patterns. The width of the halo pattern increased with the reduction of crystal size.

Cubic ice was formed at temperatures between -130 and -160C. It is estimated from the width of the diffraction rings that the cubic crystals are from 50 Å to 300 Å in diameter.

The coefficients of linear expansion along the c-axis of the hexagonal ice ranged from 50×10^{-6} to 20×10^{-6}, and were almost the same as that of the a-axis in the temperature range from 0 to -180C. The coefficients of cubical expansion ranged from 140×10^{-6} to 60×10^{-6} at temperatures from 0 to -180C. The c/a ratio of hexagonal ice sublimed from vapor at temperatures around -100C was the ideal value of 1.633 for close packing.

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13. ABSTRACT

The formation of hexagonal and cubic forms of ice was studied by the use of a cold stage in an electron microscope within the temperature range of -190 to 170°C. Ice crystal specimens were made on cold substrates, i.e., a collodion film, gold foil, or copper grid on the specimen holder of the cold stage. The structural forms of the ice were detected with the electron microscope using the selected area electron diffraction method. The hexagonal form of ice formed on the cold substrates at temperatures from -90 to -100°C. At -100 to -130°C, both hexagonal and cubic forms of ice were detected. From -130 to -160°C only cubic ice was found. At temperatures below -170°C, minute crystals of cubic ice were detected. No transformation of the structural form of ice from hexagonal to cubic or from cubic to hexagonal occurred when the temperature of the specimens was varied in the range of -90 to -160°C. The minute crystals of cubic ice formed below -160°C were transformed into larger cubic ice crystals by heating them to a temperature between -130 and -150°C. The lattice constants of hexagonal and cubic ice, and the coefficient of thermal expansion of ice were calculated from the experimental results.

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